Patented June 4, 1940 2,203,214

UNITED STATES PATENT OFFICE

2,203,214

METHOD OF MAKING ALLOYS

Ernest F. Doom, New Rochelle, N. Y., assignor to Electro Metallurgical Company, a corporation of West Virginia

No Drawing. Original application July 1, 1938, Serial No. 216,904. Divided and this application October 21, 1939, Serial No. 300,557

6 Claims. (Cl. 75—122)

This invention is a process for making alloys, and this application is a division of application Serial Number 216,904, filed July 1, 1938, jointly by Ernest F. Doom and William J. Priestley.

Columbium and tantalum are useful ingredients in many steels, notably the chromium steels. In the manufacture of such steels it is ordinarily most convenient, efficient, and economical to add columbium-tantalum group metal (by which is meant columbium or tantalum or mixtures thereof) in the form of lumps of a ferroalloy. For most purposes, such ferroalloy should contain as little carbon as possible and in no event more than 1% carbon, because columbium and tantalum form exceedingly stable and inert carbides, and it is generally the non-carbide columbium or tantalum that is desired. A typical ferrocolumbium contains about 55% columbium, about 0.5% carbon, about 7% silicon, and the remainder iron and incidental impurities. A moderately high silicon content, say 5% to 10%, is advantageous.

Although ferrocolumbium is a very useful material that has been successfully employed in the manufacture of many tons of steel, it has certain properties which are undesirable in a material to be introduced into steel baths.

The melting point of ferrocolumbium is relatively high (about 1950° C. to 2200° C. depending on the composition) and this fact makes it somewhat difficult to dissolve the alloy in a steel bath rapidly and without serious oxidation of the columbium. Ferrotantalum has a melting point even higher than that of ferrocolumbium.

Ferrocolumbium and ferrotantalum are friable, and crushing operations produce an undesirably large proportion of fines and dust having considerably less commercial value than granular and lump alloy.

It is an object of this invention to provide a new process for producing a ferroalloy containing columbium-tantalum group metal and having a lower melting point and better crushing characteristics than have heretofore been attainable in commercially useful ferrocolumbium and ferrotantalum alloy. Such a ferroalloy is one containing both chromium and columbium-tantalum group metal, the total amount of both chromium and columbium-tantalum group metal amounting preferably to between 40% and 90% of the alloy. As little as one part of chromium for each twenty parts of columbium-tantalum group metal is sufficient to impart a valuable improvement to the properties of the alloy. Larger proportions of chromium may be, and preferably are, used; but the alloy should contain at least one part of columbium-tantalum group metal for each twenty parts of chromium. In the majority of instances, a ratio of columbium-tantalum group metal to chromium between 15:1 and 1:15 will be quite satisfactory. In general, the preferred minimum amounts of chromium and columbium-tantalum group metal are 20% each, and normally neither metal need exceed 50%. For many purposes, the most useful alloys are those containing approximately equal amounts of chromium and columbium-tantalum group metal. The iron content of the alloy usefully affects the properties of the alloy and also contributes to the ease of manufacture of the material; but the iron content should not greatly exceed 60%, and is preferably much less. The carbon content should not exceed 1%, and a percentage below 0.25% is preferred for the reasons indicated above. A moderate silicon content, not exceeding 20% and preferably within the range of 3% to 8%, is desirable but not essential. Aluminum may be substituted for a part or all of the silicon, but of the two silicon is preferred. Manganese or nickel or mixtures thereof may be substituted for part of the iron. Small amounts of other elements such as titanium, copper, and tin may be introduced or may enter as incidental impurities without adversely affecting the usefulness of the alloy.

These alloys may be made by a remelting procedure using, for instance, low carbon ferrochromium and low carbon ferrocolumbium. But this method is not economical, because it requires three separate manufacturing steps each requiring equipment, time, power, and involving slag losses and adventitious increases in carbon content. Another process for making these alloys comprises the simultaneous reduction of the ores of chromium and columbium with carbon, silicon, or aluminum. One of the serious objections to this process is that either poor recovery of metallic ingredients or an impure or otherwise undesirable product will ordinarily result. The slag volume in such a process is excessive.

It is accordingly a further object of this invention to provide a process that avoids these difficulties and produces a low-carbon alloy, of any desired composition within the above-described range, economically, simply, and efficiently.

The process of the invention is based on the fact that chrome ore and other oxidic chromium materials may be reduced by silicon contained in a columbium or tantalum alloy and that, con-

versely, columbite or tantalite or other oxidic columbium-tantalum group materials may be reduced by silicon contained in a chromium alloy. Inasmuch as low-carbon high-silicon alloys and ferroalloys of chromium and of columbium-tantalum group metal can readily be made by known processes, the reductions referred to can be effected in the absence of any substantial amount of carbon. As a result, alloys containing less than 0.25% carbon may readily be obtained.

In the following description of the process, reference will be made to columbium alone, for the sake of conciseness; but it will be understood that tantalum and mixtures of columbium and tantalum may be substituted for the columbium.

The gangue content of the usual chrome ores contributes more than the gangue content of the usual columbium ores to an increase in slag content. For this reason it is preferred to start with the chromium in metallic form and to reduce columbium alone in the process.

According to a preferred procedure, a bath of molten low-carbon ferrochromium-silicon or chromium-silicon alloy is formed and provided with a slag, preferably basic, and an oxidic columbium ore or compound is added to the bath through the slag. As columbium is reduced, the metal joins the bath and silicon is oxidized and joins the slag. Although ordinarily the silicon content of the ferrochrome-silicon alloy will be selected so that the refining effect of the columbium-tantalum group oxide will be just sufficient to reduce the silicon content to that desired in the final alloy, part of the silicon may be added to the bath as silicon metal or silicon alloyed with one or more of the metals desired in the final composition.

Alternatively, a bath of molten low-carbon columbium-silicon or ferrocolumbium-silicon alloy may be treated, in similar fashion, with oxidic chromium ore or compound. Part of the silicon may be added in the form of silicon metal, ferrosilicon, chromium-silicon, or ferrochromium-silicon.

Another procedure comprises forming a small starting bath of any one or more of the metallic constituents of the desired alloy, progressively feeding into this bath a mixture containing the oxidic compound and the silicon-containing alloy, and heating the bath to keep it molten.

Instead of acting on a premelted bath with an oxidic compound, the solid reactants may be finely ground, intimately mixed, and ignited. External heating, or a suitable accelerator such as sodium nitrate, or both, may be needed in some instances to sustain the reaction; but the exothermic reaction will in any event contribute heat for the production of a molten bath.

In any of these procedures, iron may be added before, during, or after the reaction of silicon and oxidic compound, to produce either a ferroalloy or a steel. If an alloy steel is desired, an economical and simple procedure is to feed a mixture of the silicon alloy and oxide described above into a slag-covered molten bath of iron or steel.

The slags obtained in these operations will of course contain oxides of both chromium and columbium, but deliberate simultaneous additions of substantial amounts of the oxide of more than one of these elements is to be avoided, because such addition will increase the slag losses of valuable metal.

The slags containing oxides of columbium and chromium are preferably smelted with silicon or with a mixture of carbon and silica to produce a ferrochromium-columbium-silicon alloy, low in carbon, which can be substituted for part of the chromium-silicon, columbium-silicon, ferrochromium-silicon, or ferrocolumbium-silicon mentioned in the foregoing description. Alternatively, the slag may be smelted to a high carbon alloy and then refined or resmelted to lower the carbon and raise the silicon content.

In a typical experiment made in accordance with this invention, one thousand pounds of columbite and five hundred and ninety pounds of ferrochromium-silicon were ground to pass an 8 mesh screen (2.36 mm. opening) and intimately mixed with sixteen hundred pounds of lump lime, a small part of the ferrochromium-silicon being withheld from the mixture. The ferrochromium-silicon so withheld was melted in the bottom of an open-arc electric furnace to form a starting bath, and the mixture was then fed to the molten bath at regular intervals. Slag and alloy were tapped from time to time. Clean and homogeneous metal readily separated from the slag. Analyses of average samples of the starting materials and products were as follows:

Columbite	Fe—Cr—Si alloy	Fe—Cr—Cb alloy	Slag
61.8% Cb_2O_5 5.1% Ta_2O_5	34.6% Cr 50.1% Si	28.6% Cr 43.2% Cb 0.7% Ta	0.3% Cr 7.5% Cb_2O_5
14.1% CaO	14.3% Fe	18.1% Fe 5.4% Si	
5.8% FeO	0.04% C	1.8% Mn 0.26% C	
2.2% MnO			

64% of the columbium and 90% of the chromium were recovered in metallic form.

Although in the foregoing description preferred conditions have been described in some detail, economic and other practical considerations may on occasion dictate a departure from such conditions. Accordingly, the detailed description is to be regarded as illustrative of the invention and not as imposing limitations not required by the state of the art and the scope of the claims.

I claim:

1. Process for producing a low-carbon alloy containing chromium metal and columbium-tantalum group metal which comprises heating an oxidic compound of one of the said metals with a silicon-containing alloy of the other of said metals to a reaction temperature; reducing said compound, with said silicon, to metallic form; and coalescing the resulting metals to form a melt of the desired alloy.

2. Process for producing a low carbon alloy of chromium and columbium which comprises heating chrome ore with a low-carbon high-silicon columbium alloy to a reaction temperature, reacting the ore with the silicon of the alloy, and coalescing the chromium so produced with the columbium alloy.

3. Process for producing a low-carbon ferroalloy of chromium and columbium which comprises forming a molten bath of low-carbon high-silicon ferrocolumbium covered with a basic slag, and adding chrome ore to said bath through the slag.

4. Process for producing a low-carbon alloy of chromium and columbium which comprises heating columbite ore with a low-carbon high-silicon chromium alloy to a reaction temperature, reacting the ore with the silicon of the alloy, and

coalescing the columbium so produced with the chromium alloy.

5. Process for producing a low-carbon ferroalloy of chromium and columbium which comprises forming a molten bath of low-carbon high-silicon ferrochromium alloy covered with a basic slag, and adding columbite ore to said bath through the slag.

6. Process for producing a low-carbon alloy containing chiefly chromium and columbium-tantalum group metal which comprises heating an oxidic compound of one of the said metals with a silicon-containing alloy of the other of said metals to a reaction temperature; reducing said compound, with said silicon, to metallic form; coalescing the resulting metals to form a melt and an overlying slag containing oxides of chromium and columbium-tantalum group metal; separating the metal from the slag; treating said slag with silicon to produce a silicon-containing alloy; and reducing another portion of said oxidic compound with the last-mentioned silicon-containing alloy.

ERNEST F. DOOM.